

## CPP 85: Focus: Polymers under confinement I

Polymers under confinement are ubiquitous in nature and technology, ranging from the crowded interior of biological cells to thin polymer coatings. Confinement can either be imposed externally or it can emerge spontaneously through the self-organization of the constituents. Confinement decreases substantially the available degrees of freedom, and can lead to a wealth of intriguing phenomena nonexistent in bulk systems. Important aspects include, e.g., the size, shape and rigidity of the bounding geometry, and the properties and packing fraction of the enclosed particles. In this focus session, we will explore the structure formation, dynamics, and other aspects of these systems. Organized by: Arash Nikoubashman (Johannes Gutenberg Universität Mainz).

Time: Thursday 9:30–12:45

Location: ZEU 222

**Invited Talk** CPP 85.1 Thu 9:30 ZEU 222

**Molecular view on polymers adsorbed on nanoparticle surfaces** — MOZHDEH ABBASI<sup>1</sup>, SOL MI OH<sup>2</sup>, SO YOUN KIM<sup>2</sup>, and ●KAY SAALWÄCHTER<sup>1</sup> — <sup>1</sup>Inst. f. Physik - NMR, Martin-Luther-Univ. Halle-Wittenberg, Halle (Saale), Germany — <sup>2</sup>School of Energy and Chemical Engineering, UNIST, Ulsan, Republic of Korea

The reinforcement effect of nanoparticles in a polymer matrix is related to an interphase with modified properties [1]. Previous results support a consensus picture of adsorbed components with locally increased T<sub>g</sub> and gradient zone of a few nm [2]. This talk focuses on more recent results, mostly obtained by proton low-resolution NMR as a probe of the segmental dynamics, that challenge the generality of this picture. In the system poly(ethylene oxide)-silica, we do find strongly immobilized (yet intrinsically mobile) components forming a layer of up to 2 nm thickness around the particles [3], but the layer thickness is temperature-independent and is governed by a non-equilibrium process in dependence of end groups [3] and preparation conditions [4], and also of the curvature of the particles. Spin-diffusion NMR experiments, which probe the size of nanometric domains with distinct mobility, indicate that the smooth-mobility-gradient picture of the “glassy layer” must be replaced by a scenario ruled by dynamic heterogeneities associated with the increased glass transition [5].

[1] A. Mujtaba et al., ACS Macro Lett. 2014, 3, 481 [2] A. Papon et al., Phys. Rev. Lett. 2012, 108, 065702 [3] Y. Golitsyn et al., J. Chem. Phys. 2017, 146, 203303 [4] S. M. Oh et al., Phys. Rev. Lett. 2019, 123, 167801 [5] H. Schneider et al., Macromolecules 2017, 50, 8598

CPP 85.2 Thu 10:00 ZEU 222

**Structural details of polymer grafted nanoparticles: Insights from coarse-grained molecular dynamics simulations** — ●JIARUL MIDYA<sup>1</sup>, MICHAEL RUBINSTEIN<sup>2</sup>, SANAT K. KUMAR<sup>3</sup>, and ARASH NIKOUBASHMAN<sup>1</sup> — <sup>1</sup>Johannes Gutenberg University of Mainz, Mainz, Germany — <sup>2</sup>Duke University, Durham, United States — <sup>3</sup>Columbia University, New York, United States

Polymer grafted nanoparticles (GNPs) are promising materials with a wide range of applications in drug delivery, gas separation, photonic and electric materials. In this work, the structural properties of GNPs are studied via coarse-grained molecular dynamics simulations. We systematically vary the degree of polymerization at fixed grafting density, and study in detail the shape and size of the GNPs, the interpenetration between the grafted polymers and their conformations. We then compare these properties to the ones of pure polymer melts to assess the effect of confinement. We observe that the amount of chain-sections in the interpenetration zone is proportional to the length of the grafted chains,  $N_g$ , whereas, the brush height follows a power-law like behavior  $h \sim N_g^\alpha$ , where exponent  $\alpha$  decreases from a value close to one to the limiting value of 1/3 with the increase of  $N_g$ . To understand the scaling behavior of  $h$  we provide an empirical form, involving the length of the grafted polymers and the core size of the GNPs, which explains our simulation results.

CPP 85.3 Thu 10:15 ZEU 222

**The role of entanglements in non-equilibrium polymer films** — ●HSIAO-PING HSU and KURT KREMER — Max Planck Institute for Polymer Research, Mainz, Germany

Equilibrating polymer melts containing highly entangled large polymer chains in confinement or with free surfaces is a challenge for computer simulations. We approach this problem by first studying polymer melts based on the soft-sphere coarse-grained model confined between two soft repulsive walls at a distance compatible with the simulation box of bulk melts in equilibrium and keeping the periodic boundary conditions

in the directions parallel to the walls. Then we apply the backmapping methodology to reinsert the underlying microscopic details of the bead-spring model. Turning off the wall potential, the monomer density of confined polymer melts in equilibrium is kept at the bulk density even near the walls. By removing the walls we can study free standing, highly entangled polymer films. We start to stretch the initial films into two directions parallel to the free surfaces, and shrink the thickness of films, while keeping the surface pressure at zero. Finally, we quench the thin polymer films below the glass transition temperature to freeze the structure and analyze the local morphology.

CPP 85.4 Thu 10:30 ZEU 222

**Growth Kinetics and Molecular Mobility of Irreversibly Adsorbed Layers in Thin Films of P2VP and PVME** — ●MARCEL GAWEK, SHERIF MADKOUR, ANDREAS HERTWIG, and ANDREAS SCHÖNHALS — Bundesanstalt für Materialforschung und -prüfung, Unter den Eichen 87, 12205 Berlin

In well-annealed thin polymer films, with non-repulsive polymer/substrate interactions, an irreversibly adsorbed layer is formed. These adsorbed layers have shown enormous potential for technological applications. Due to the hard accessibility of these layers, their growth kinetics and molecular dynamics are still not fully understood. Here, the irreversibly adsorbed layers of Poly(2-vinylpyridine) (P2VP) and Poly(vinyl methyl ether) (PVME) thin films are revealed by solvent-leaching experiments. The growth kinetics of these layers is investigated as a function of original film thickness and annealing times. The thickness, topography and quality of the adsorbed layer is determined with Atomic Force Microscopy (AFM) and spectroscopic ellipsometry. Additionally, the molecular mobility of the adsorbed layer is investigated with Broadband Dielectric Spectroscopy (BDS). A recently developed nanostructured capacitor (NSC) is employed to measure the adsorbed layers with a free surface layer depending on annealing and solvent-leaching time. The results are quantitatively compared and discussed with respect to recently published work.

CPP 85.5 Thu 10:45 ZEU 222

**Kinetically trapped chiral structures of diblock copolymers in cylindrical confinement** — ●LUDWIG SCHNEIDER, GEORG LICHTENBERG, and MARCUS MÜLLER — Institut für Theoretische Physik, Georg-August Universität Göttingen

Reproducibly manufacturing morphologies of diblock copolymers inside cylindrical confinements is a long-standing question in directed self-assembly. It has been explored both in experiments and simulations. For non-neutral cylinder walls, it is expected that concentric lamellae are formed.

However, we discover interesting long-lived helical structures via large-scale Single-Chain-in-Mean-Field (SCMF) simulations. The requirements for these structures are neutral interactions between the confinement and the two polymer species and an incommensurable cylinder length with the natural lamellar spacing.

We believe the structures to be meta-stable but long-lived. The kinetic pathway after a spinodal decomposition consistently drives the morphology towards the helical structures. After the meta-stable structure is formed, it is long-lived because a transition towards equilibrium requires a global remodeling of the morphology – accompanied by a high free-energy barrier.

**30 min. break**

**Invited Talk** CPP 85.6 Thu 11:30 ZEU 222

**Nonequilibrium Properties of Polymers in Confinement** — ●ROLAND G. WINKLER — Theoretical Soft Matter and Biophysics,

Institute for Advanced Simulation, Forschungszentrum Jülich, 52428 Jülich

The interplay between polymer conformational degrees of freedom, confinement, and nonequilibrium forces results in intriguing structural and dynamical properties [1]. The out-of-equilibrium state can either be achieved by well established external fields, such as electric, magnetic, and flow fields, or by active forces, as for polar filaments of the cytoskeleton of a cell. Moreover, in living cells, nonthermal fluctuations (colored noise), induced by ATP-powered enzymes, are expected to play a major role in DNA organization and for the dynamics of the chromatin in the nucleus. The novel emerging phenomena of active soft matter render them a promising class of new materials [2]. We studied the properties of soft colloids, like linear polymers and star polymers under flow, specifically the interplay between flow, polymer conformations, and hydrodynamic interactions. In particular, we find that the latter strongly affect the properties of polymers in a channel [3]. For "active" polymers, we find that their internal degrees of freedom strongly affect the conformations, and in particular, the phase behavior. [1] R. G. Winkler, D. A. Fedosov, G. Gompper, *Curr. Opin. Colloid Interface Sci.* 19, 594 (2014) [2] R. G. Winkler, J. Elgeti, G. Gompper, *J. Phys. Soc. Jpn.* 86, 101014 (2017) [3] R. Chelakkot, R. G. Winkler, G. Gompper, *EPL* 91, 14001 (2010)

CPP 85.7 Thu 12:00 ZEU 222

**Confined polymer dynamics: an effective model for polymer transport in porous materials** — ●PAOLO MALGARETTI — Max Planck Institute for Intelligent Systems

We study the translocation of polymers across varying-section channels. Using systematic approximations, we derive a simplified model that reduces the problem of polymer translocation through varying-section channels to that of a point-like particle under the action of an effective potential. Such a model allows us to identify the relevant parameters controlling the polymer dynamics and, in particular, their translocation time. By comparing our analytical results with numerical simulations we show that, under suitable conditions, our model provides reliable predictions of the dynamics of both Gaussian and self-avoiding polymers, in two- and three-dimensional confinements. Moreover, both theoretical predictions, as well as Brownian dynamic results, show a non-monotonous dependence of polymer translocation velocity as a function of polymer size, a feature that can be exploited for polymer separation.

[1] V. Bianco, P. Malgaretti *JCP* 145, 114904 (2016)

CPP 85.8 Thu 12:15 ZEU 222

**Structure and Dynamics of Single-Chain Nanoparticles in Crowded Environments: A Combined SANS & NSE Study** —

●TIMO BRÄNDEL<sup>1</sup>, PAULA MALO DE MOLINA<sup>2</sup>, JULIAN OBERDISSE<sup>3</sup>, INGO HOFFMANN<sup>4</sup>, LIONEL PORCAR<sup>4</sup>, JOSETXO POMPOSO<sup>2</sup>, ARANTXA ARBE<sup>2</sup>, and JUAN COLMENERO<sup>1,2</sup> — <sup>1</sup>Donostia International Physics Center, San Sebastian, Spain — <sup>2</sup>Centro de Fisica de Materiales, San Sebastian, Spain — <sup>3</sup>Laboratoire Charles Coulomb, Montpellier, France — <sup>4</sup>Institut Laue-Langevin, Grenoble, France

Very recently, single-chain nanoparticles (SCNP) have been granted lots of attention in different fields of physical and chemical science. Due to their sparse-like structure, SCNP are often considered as versatile model-systems for a very interesting class of proteins, namely intrinsically disordered proteins (IDP). The synthesis of SCNP is carried out by intra-molecular crosslinking of single polymer chains by various cross-linking reactions. Therefore, SCNP are usually synthesized and investigated in strongly diluted solutions, but IDP exist rather under crowded conditions like most proteins. Hence, the effect of macromolecular crowding on SCNP is very important. Our study uses the outstanding possibilities of neutron scattering to investigate the effect of crowding on the structure and dynamics of SCNP. To address this issue, PS based SCNP are investigated in a completely contrast-matched matrix of deuterated linear PS chains by means of SANS and NSE. Important effects of the crowded environment on structural properties of the SCNP are observable and the internal dynamics are considerably slowed down compared to the dilute state.

CPP 85.9 Thu 12:30 ZEU 222

**Glassy behavior of cyclic polymers in a confinement** —

●STANARD MEBWE PACHONG<sup>1</sup>, JAN SMREK<sup>2</sup>, and KURT KREMER<sup>1</sup> — <sup>1</sup>Max Planck Institute for Polymer Research, Mainz, Ackermanweg 55128, Germany — <sup>2</sup>Faculty of Physics, University of Vienna, Boltzmanngasse 5, A-1090 Vienna, Austria

The behavior of a dense non-concatenated ring polymers within a confined spherical geometry is investigated. By increasing the temperature of a part of each chain, the activity based segregation is observed. We showed that introducing the activity in the system changes the topological state of the chains irrespective of the constraint imposed by the confinement. The dynamics and size analysis indicate that the chains swell when a part of it have its temperature increased. The swelling allow mutual threading of ring. We conclude that the enhance of mutual threading between chains due to thermal anisotropy, together with the chains' topological state drive the system into a kinetically arrested state.